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TITLE XAFS ANALYSIS IN THE ANHARMONIC LIMIT: APPLICATION TO HI-Te  
SUPERCONDUCTORS AND FERROSILICATES

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# **XAFS ANALYSIS IN THE ANHARMONIC LIMIT; APPLICATION TO HI-T. SUPERCONDUCTORS AND FERROSILICATES**

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## **INTRODUCTION**

The effect of lattice vibrations in XAFS, reflected in the relative motion of atomic pairs, is usually taken into account by the use of a harmonic Debye-Waller factor. However such treatment is known to be invalid in several situations of interest, *e.g.* superionic conductors,[1] metals near the melting point,[2] etc. The use of a harmonic treatment in these situations leads to results in conflict with those obtained using diffraction techniques.[2,3] The effect of small anharmonicity has been discussed by several authors, [1-3] finding that in some cases the correction of the harmonic Debye-Waller factor by the first few cumulant expansion terms suffices to reconcile XAFS and diffraction results. However, even in situations where anharmonicity is moderate or when the single particle potentials used to describe the lattice dynamics of the system exhibit nearby minima the cumulant expansion breaks down.[4] In order to treat the problem of high anharmonicity, we have generalized the formulation for the exact XAFS thermal average in terms of a RDF,[3] to the quantum mechanical regime, and implemented this formulation in the fitting of XAFS data. This approach permits the treatment of highly anharmonic motion that can not be analyzed using cumulant expansions of the Debye-Waller factor.[4]

## **XAFS IN THE ANHARMONIC LIMIT**

As a starting point, we consider the single scattering XAFS formula for a static bond [5]. In order to take into account the relative motion of a given atomic pair

we perform an statistical average of  $\chi$ :

$$\langle \chi \rangle = \text{tr}[\rho \chi] \quad (1)$$

Here,  $\rho$  denotes the density matrix associated with the single particle Hamiltonian,  $H = p^2/2m + V(z)$ , which describes the relative pair motion,  $z$  denotes the displacement relative to the average pair distance  $R$ , i.e.,  $r = R + z$ , and we consider only motion along the bond direction.  $\chi$  is taken to be an operator due to its dependence on the parameter  $z$ . The statistical average can be expressed in terms of the wave functions  $\{\Psi_i(z)\}$ , derived from the Hamiltonian  $H$ :

$$\langle \chi \rangle = \frac{\sum_i \int dz |\Psi_i(z)|^2 e^{-\beta E_i} \chi(k, r)}{\sum_i e^{-\beta E_i}} \quad (2)$$

$E_i$  denotes the  $i^{\text{th}}$  eigenvalue of the Hamiltonian, and  $\beta = 1/k_B T$  where  $k_B$  is the Boltzmann constant and  $T$  the temperature of the system.

We determine the wavefunctions  $\{\Psi_i(z)\}$  by solving the Schrödinger equation using the reduced mass for the atomic pair of interest, and an anharmonic model potential  $V(z)$ , that is characterized in terms of parameters determined by fitting  $\langle \chi \rangle$  to experiment. We note that  $V(z)$  represents the effect of all surrounding atoms in the relative motion of the pair. Since correlations between different pairs are neglected, this treatment is analogous to the Einstein approximation commonly used in XAFS analysis.

We perform a non-linear squares fit in the  $k$  region of interest, using as parameters to be determined:  $R$  and the potential parameters, at the temperature of interest. The number of atoms  $N$  is held fixed to the crystallographic determined value. The XAFS amplitude and phase functions are determined using: reference compounds, theoretical calculations, or (if anharmonicity is negligible at low temperatures) the low temperature data. The RDF,  $g(z)$ , is defined as:

$$g(z) = \frac{\sum_i |\Psi_i(z)|^2 e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \quad (3)$$

Thus, Eq. 2 can be written in a compact form as:

$$\langle \chi \rangle = \int dz g(z) \chi(k, r(z)) \quad (4)$$

If all the temperatures of interest are far above low energy eigenvalues of  $H$  ( $T \gg E_0$ ), then one can resort to a classical treatment. In this case  $g(z)$  is given by:

$$g(z) = e^{-\alpha |z|} / \int e^{-\alpha |z|} dz \quad (5)$$

The RDF,  $g(z)$ , gives a complete description of the pair motion and one can extract the temperature behavior of any moment of interest from it, i. e.:

$$\langle z^n \rangle = \int dz g(z) z^n \quad . \quad (6)$$

## HIGH-TEMPERATURE SUPERCONDUCTORS

We have employed the mentioned formalism to the analysis of axial oxygen (O4) contributions to polarized Cu K-edge XAFS in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . The coupling of valence fluctuations in the Cu atoms ( $\text{Cu}^{+2} \leftrightarrow \text{Cu}^{+1}$ ) to vibrations of the O4 atom leads to anharmonic potentials for the motion of O4.[6] We used several model potentials to fit the XAFS, finding the best fit for the model potential:  $V(z) = a(z-z_0)^2, (z < 0); \quad b(z-z_1)^2, (z > 0)$ . In Fig. 1a we present the potential and RDF for the Cu1-O4 bond for different temperatures obtained from the fits. These fits were performed on Fourier filtered first shell contributions  $k^3\chi$  in the range  $4 \leq k \leq 14 \text{ \AA}^{-1}$ , with amplitude and phase functions extracted from  $\text{La}_2\text{CuO}_4$ , using as fitting parameters  $a, b, z_0, z_1$ , and the equilibrium bond distance  $R$ . The fits show the presence of an elastic anomaly associated with the onset of superconductivity, signaled by a sharp increase in the tunnelling frequency between the two well sites (Fig. 1b).[7] Fits using harmonic potentials lead to errors in the Cu-Cu distance of more than  $0.1 \text{ \AA}$  and erratic behavior in other fitting parameters.

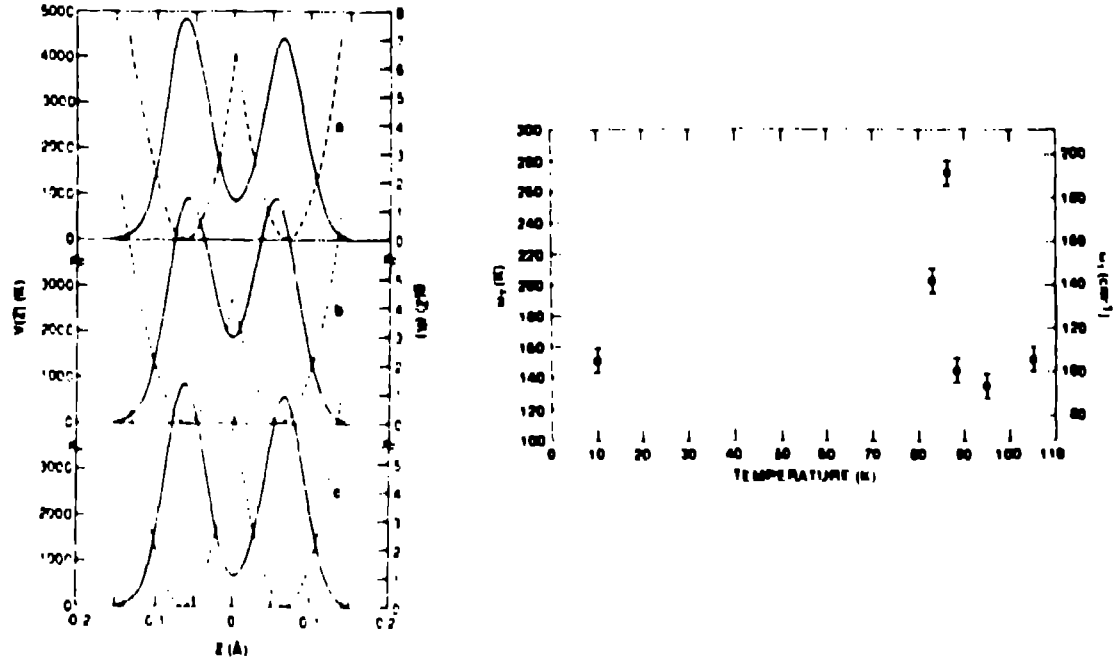


Figure 1a. Potential (dashed line) and RDF (solid line) for axial oxygen in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  at a) 10K, b) 86K, and c) 105K. Figure 1b. Tunnelling frequency between the two well sites in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  as a function of temperature.

## FERROSILICATES AT HIGH TEMPERATURES

We have also employed this method to the analysis of Fe K-edge XAFS O contributions in andradite ( $\text{Fe}_2\text{Ca}_3\text{Si}_3\text{O}_{12}$ ) for temperatures  $80 \leq T \leq 1073\text{K}$ . A model potential  $V(r) = U[(r/r_0)^{12} - 2(r/r_0)^8]$  was used, determining  $U$  by fitting to experiment at  $1073\text{K}$ , while  $r_0$  was allowed as a function of temperature. These fits were performed on Fourier filtered first shell contributions  $k^3\chi$  in the range  $3 \leq k \leq 11\text{\AA}^{-1}$ , using amplitude and phase functions extracted from the data at  $80\text{K}$ .<sup>[8]</sup> The RDF for different temperatures is shown in Fig. 2a. The fits reproduce crystallographic distances (See Fig. 2b), and explain the apparent bond contraction obtained using harmonic fits.<sup>[8]</sup>

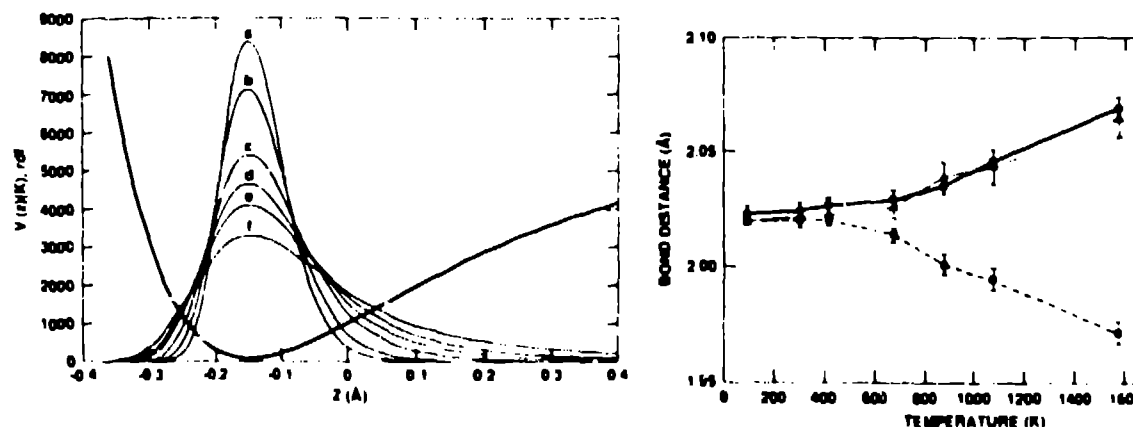


Figure 2a. Potential (wide line) and RDF (thin line) from fits to Fe-O XAFS in andradite at a)  $300\text{K}$ , b)  $413\text{K}$ , c)  $673\text{K}$ , d)  $873\text{K}$ , e)  $1073\text{K}$ , and f)  $1573\text{K}$  (from calculated XAFS). Figure 2b. Fe-O distance extracted from diffraction experiments (thin line), XAFS anharmonic fits (wide line), and c) XAFS harmonic fits. (dashed line)

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